STUDIES IN ADSORPTION ON GELS.*

I. A Comparative Study of Selective Adsorption from Binary Mixtures of Liquids on Gels of Silica, Alumina and Ferric Oxide.

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SELECTIVE adsorption on silica gel and activated carbon from binary mixtures of liquids has been studied by several workers. Patrick and Jones,[16] working with silica gel, have suggested that the order of increase of adsorption of the solute from a series of solvents is the same as the order of the decrease of the solubility of the solute in the solvents. Jones and Outridge[9] have noticed selective adsorption of *n*-butyl alcohol from benzene-*n*-butyl alcohol-silica gel system. Bartell and co-workers[1,2,3] have worked with carbon and silica gel and explained selective adsorption in relation to adhesion tension data. B. S. Rao[19] after making a study of selective adsorption from various mixtures on silica gel has pointed out how the nature of the liquids employed determines selective adsorption. Doss and B. S. Rao,[6] in a study of " Apparent " and " True " adsorption functions, have discussed the factors underlying selective adsorption. The present paper deals with the influence of gel surface on selective adsorption from liquids. Gels of alumina and ferric oxide were employed in this investigation and the results compared with those obtained on silica gel by B. S. Rao.[19]

Experimental.

Preparation of alumina gel.—To a 0·3 N solution of chemically pure aluminium sulphate kept at 25° C. was added ammonium hydroxide (0·3 N) in a thin stream, the solution being vigorously stirred. According to Yoe[21] the adsorptive capacity of alumina gel is greater the lower the temperature at which it is precipitated. An excess of ammonium hydroxide corresponding to 10% of what was required for complete reaction was employed. The alumina precipitate was filtered over cloth, and washed with distilled water till the filtrate was free from sulphate. It was then dried at 90° C. for 24

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hours and the resulting gel which was hard was graded into various sizes. Granules 1 to 2 mm. in diameter were used in the investigation.

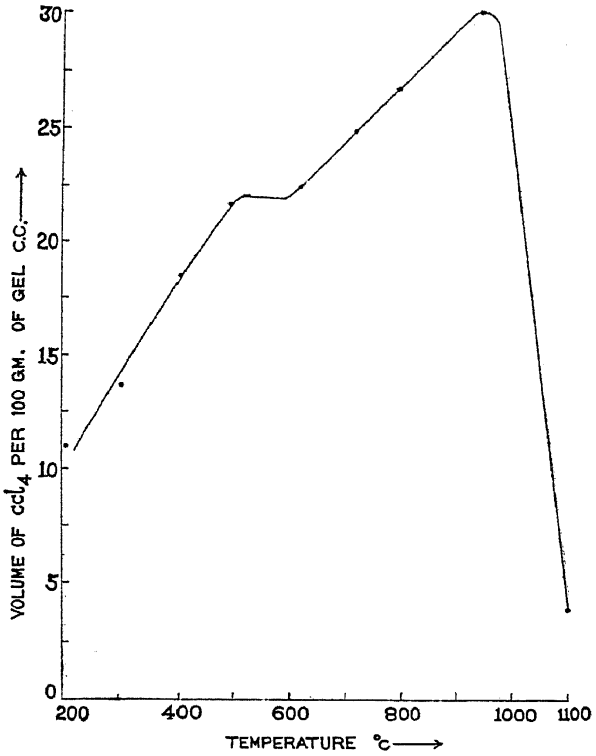
Preparation of ferric oxide gel.—Ferric oxide gel was prepared by mixing 0·5 N ferric chloride solution with 0·5 N ammonium hydroxide solution there being a 25% excess of the latter, the procedure being the same as in the case of alumina gel. The gel was hard and was dark-red in colour.

Activation of alumina gel.—There has been wide variation in the temperature employed by earlier workers in the activation of alumina gel. Chowdhury and Bagchi[5] have activated the gel at 300°–400° C., Perry[18] at 200° C., Munro and Johnson[13,14,15] at 300°–400° C., Wood [20] at 1000° C., Dunstan[7] at 600–700° C. and Bayley[4] at 550° C. An investigation of the optimum temperature of activation of the gel was therefore carried out, employing temperatures ranging from 200° to 1100° C. A current of dry and carbon dioxide-free air was passed over the gel during activation. The adsorptive capacity of the activated gel was determined by passing over the gel kept at 25° C. in a weighed U tube, a current of dry air saturated with carbon tetrachloride vapour, until there was no further increase in the weight of the tube. The volume of carbon tetrachloride adsorbed in each case may be considered to indicate the total volume of the capillaries in the activated gel. Results obtained are shown in Table I.

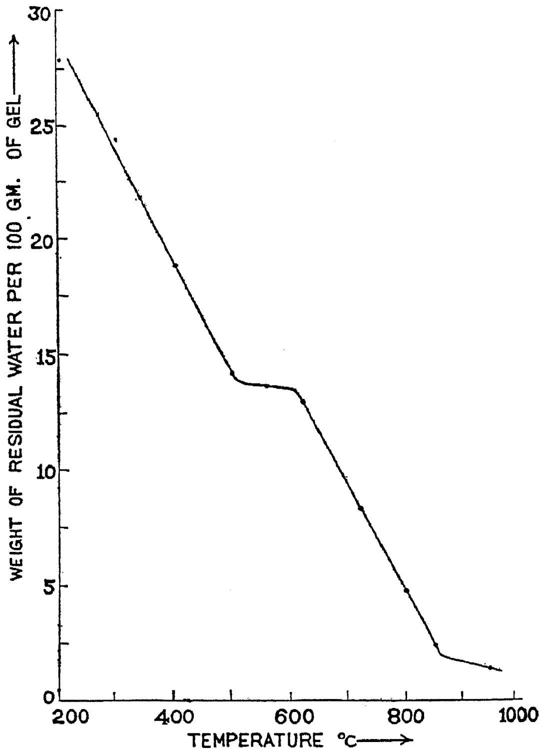
TABLE I.

Temperature of activation of alumina gel in °C.	Volume in c.c. adsorbed per 100 gm. of gel	Weight of residual water in 100 gm. of gel
205	10·97	27·81
305	13·69	24·32
405	18·45	18·83
500	21·58	14·10
620	22·43	12·90
720	24·87	8·25
800	26·62	4·72
850	28·30	2·30
950	29·96	1·47
1100	3·89	..

The relation between the temperature of activation and the volume of carbon tetrachloride adsorbed is represented in Graph 1 and the relation between the temperature and percentage of residual water in Graph 2. Gel activated at 950° C. seems to have the largest capillary space. A safe temperature for effective activation would however be 800° C. Repeated revival of spent gel by activation at 800° C. had no deleterious effect on the capillary space.



GRAPH 1.



GRAPH 2.

The break in the curve in Graph 2 in the neighbourhood of 500° C. is of interest. Between the temperatures 500° C. and 620° C, the gel seems to lose water with difficulty. It is seen also from Table I that at 500° C. increase of temperature of activation to 600° C. does not cause a corresponding increase in capillary space. These observations seem to indicate that part of the water in alumina gel is in the form of a hydrate. It is significant that the phenomenon noticed above occurs when the gel has 14 per cent. water while the monohydrate of alumina has 15 per cent. water.

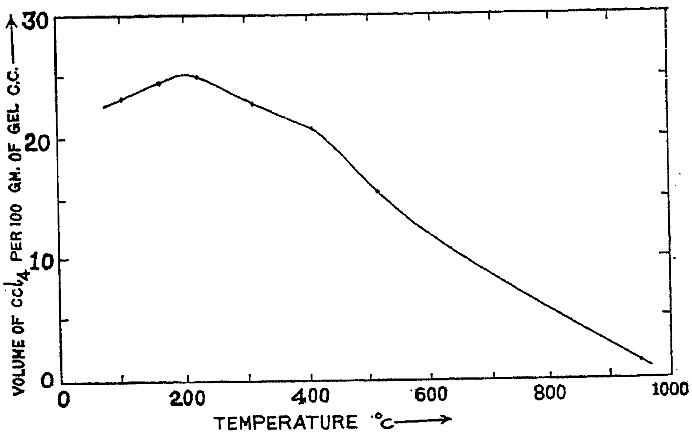
At 900° C. there is a sharp change in the curve in Graph 2. When the temperature of activation is raised beyond 950° C. the capillaries get destroyed and the gel turns chalky white. Structural changes in alumina at

900° C. have been noticed by earlier workers who found the reaction exothermic. The phenomenon has been called calorescence, J. W. Mellor.[12]

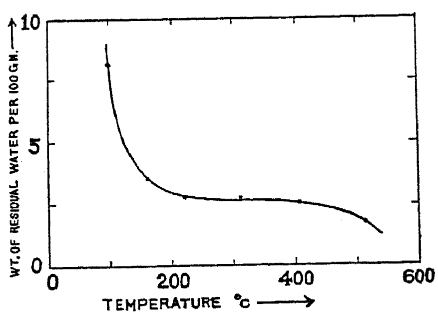
Activation of ferric oxide gel.—Lambert and Clark,[10,11] in studying adsorption hysteresis with ferric oxide, have activated the gel at 170° C. Perry[17] uses in his work ferric oxide gel activated at 230° C. Emmet and Love[8] have found that ferric oxide activated at 550° C. has for water vapour one-fourth the adsorption efficiency of gel activated at 300° C. The optimum temperature of activation for ferric oxide was determined by the method employed for alumina gel. The results are shown in Table II.

TABLE II.

Temperature of activation of ferric oxide gel in °C.	Volume in c.c. of carbon tetrachloride adsorbed per 100 gm. of gel	Weight of residual water in 100 gm. of gel
100	23·10	8·19
160	24·56	3·51
220	25·00	2·72
310	22·86	2·90
405	20·82	2·61
510	15·61	1·74
950	1·15	..



GRAPH 3.



GRAPH 4.

With reference to Graph 3, gel activated at 220° C. has the maximum adsorptive capacity and the adsorptive capacity diminishes as the temperature of activation is increased. A temperature of 180°–200° C. seems to be most suitable for activation of ferric oxide. Relation between the temperature of activation and the percentage of residual water in the gel is shown in Graph 4. As with alumina, repeated revival of spent gel did not affect the adsorptive capacity.

Adsorption experiments.—The organic liquids employed in the work were purified by standard methods. The following mixtures were used:

1. Ethyl alcohol and benzene.
2. Ethyl alcohol and carbon tetrachloride.
3. Ethyl alcohol and water.
4. Water and pyridine.
5. Benzene and carbon tetrachloride.

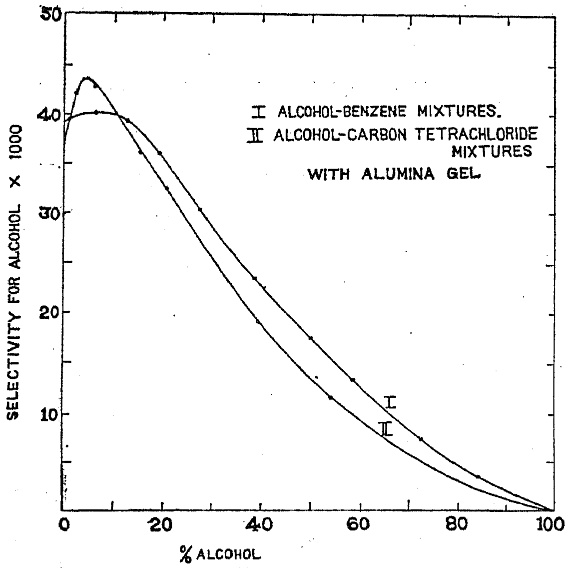
Procedure.—A known weight (7 to 8 gm.) of the activated gel was dropped into a small "sample tube" containing a known weight (4 to 5 gm.) of the binary mixture. To avoid heat effects during adsorption the tube was cooled in ice. Samples of the liquid were withdrawn for analysis after the tube had been kept in a thermostat at 25° C. for 12 hours. The composition of the liquid was determined with the aid of a Pulfrich refractometer.

Selective adsorption on the gel is expressed by the term "Selectivity" given by the relation,

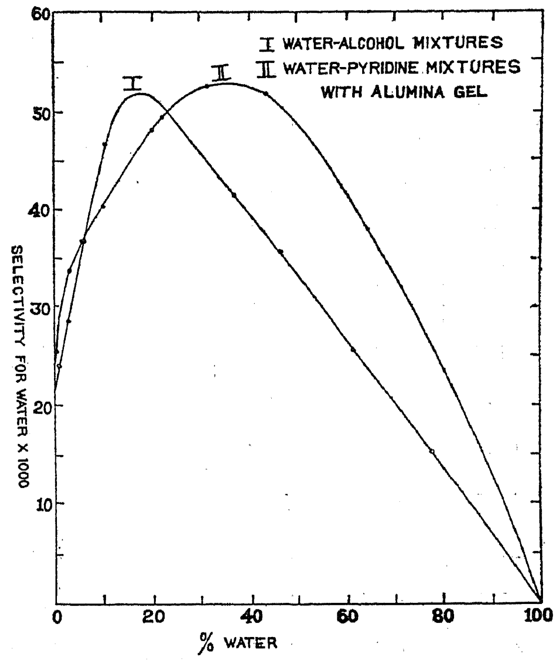
$$S = \frac{w\,(c_i - c_l)}{100\,m}$$ (B. S. Rao[19])

where S = Selectivity.
w = weight of the liquid mixed with the gel.
c_i = the initial composition of the liquid mixture in weight per cent.
c_l = the final composition of the liquid mixture in weight per cent.
m = weight of the gel.

The results obtained are given in Tables III and IV and the selectivity-concentration curves in Graphs 5 to 10.



GRAPH 5.



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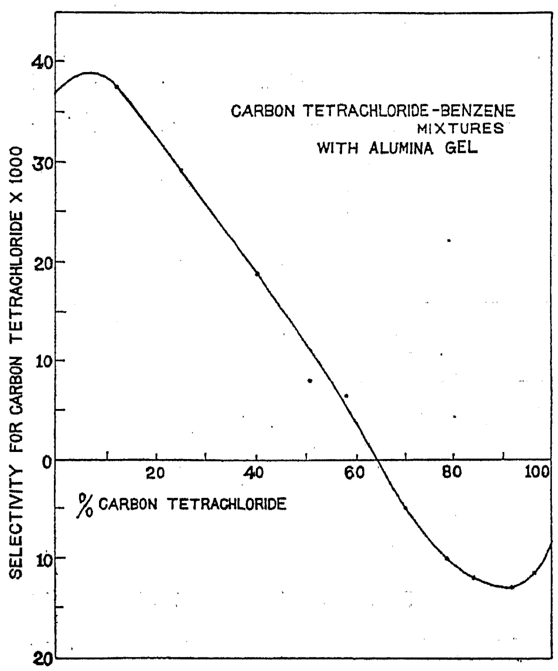

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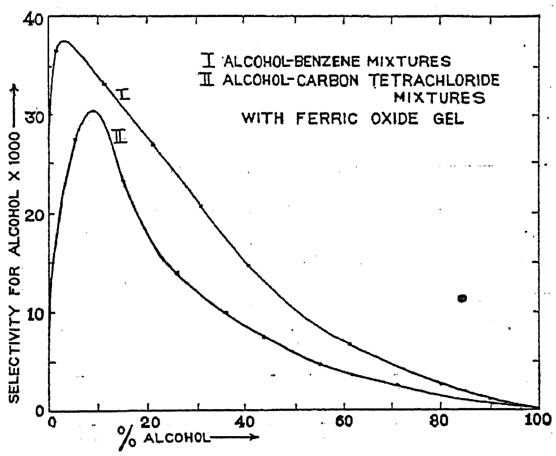
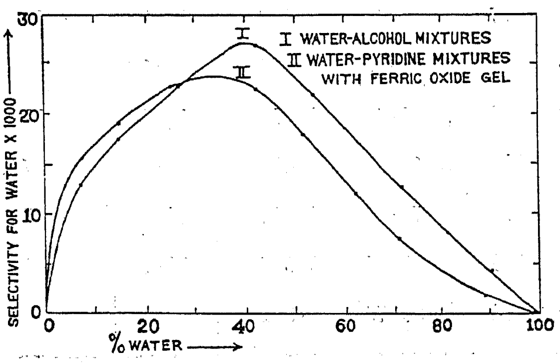


GRAPH 8.



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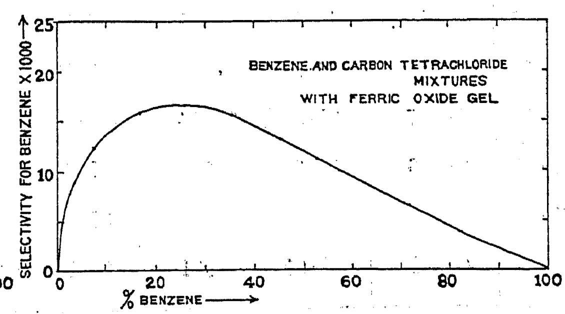

GRAPH 10.

TABLE III. *Selective adsorption on alumina gel from binary mixtures.*

EtOH and C_6H_6		EtOH and CCl_4		EtOH and H_2O		H_2O and Pyridine		C_6H_6 and CCl_4	
p.c. of Et OH	Selectivity for EtOH	p.c. of Et OH	Selectivity for EtOH	p.c. of H_2O	Selectivity for H_2O	p.c. of H_2O	Selectivity for H_2O	p.c. of CCl_4	Selectivity for CCl_4
C_l		C_l		C_l		C_l		C_l	
1·10	0·039	2·40	0·042	1·15	0·024	0·95	0·026	12·25	+0·037
6·15	0·040	6·60	0·043	3·60	0·029	3·45	0·034	25·30	+0·029
12·35	0·039	9·15	0·040	6·70	0·037	6·30	0·037	40·70	+0·019
19·15	0·036	15·70	0·036	10·85	0·047	10·25	0·040	50·80	+0·008
27·70	0·030	20·75	0·032	27·30	0·029	19·80	0·048	57·95	+0·006
38·50	0·024	30.70	0·024	37·00	0·041	21·65	0·050	69·80	—0·005
49·55	0·017	39·65	0·019	46·90	0·036	31·35	0·053	78·65	—0·010
58·40	0·013	53·95	0·012	61·65	0·026	43·20	0·052	84·00	—0·012
72·15	0·008	77·00	0·001	78·00	0·015	64·50	0·038	91·65	—0·013
83·80	0·004							96·50	—0·011

TABLE IV. *Selective adsorption on ferric oxide gel from binary mixtures.*

EtOH and C_6H_6		EtOH and CCl_4		EtOH and H_2O		H_2O and Pyridine		C_6H_6 and CCl_4	
p.c. of Et OH	Selectivity for EtOH	p.c. of EtOH	Selectivity for EtOH	p.c. of H_2O	Selectivity for H_2O	p.c. of H_2O	Selectivity for H_2O	p.c. of C_6H_6	Selectivity for C_6H_6
C_l		C_l		C_l		C_l		C_l	
1·50	0·037	5·65	0·028	7·10	0·013	7·65	0·016	7·95	0·012
11·25	0·033	14·95	0·023	14·25	0·018	14·66	0·019	16·85	0·016
21·25	0·027	25·70	0·014	26·66	0·013	24·90	0·023	26·00	0·017
30·70	0·021	35·33	0·010	32·70	0·027	33·60	0·024	35·50	0·016
40·35	0·015	43·35	0·008	42·70	0·027	42·35	0·022	45·50	0·013
49·00	0·014	54·90	0·005	53·85	0·022	51·40	0·018	52·90	0·011
60·85	0·007	61·90	0·004	63·30	0·013	62·45	0·012	60·50	0·007
69·25	0·006	71·00	0·003	71·40	0·013	70·90	0·007	71·90	0·007
80·00	0·003	82·00	0·003	81·00	0·008	81·60	0·004	81·70	0·004
89·35	0·001	90·60	0·001	90·30	0·004	88·75	0·002		

Discussion.

Alcohol is selectively adsorbed on alumina and ferric oxide gels from alcohol-benzene and alcohol-carbon tetrachloride mixtures, over the entire range of concentrations. This is analogous to the behaviour of silica gel as studied by B. S. Rao[19] and Doss and B. S. Rao.[6] Alumina and ferric oxide, however, differ from silica gel in their behaviour towards alcohol-water mixtures. Silica gel gives the S-type selectivity-concentration curve, there being selective adsorption of alcohol in dilute alcoholic solutions and selective adsorption of water from concentrated solutions, while alumina and ferric oxide gels give the U-type curves indicating selective adsorption of water at all concentrations.

Silica gel gives with pyridine-water mixtures the S-type curve (B. S. Rao[19] and Doss and B. S. Rao[6]), with alumina and ferric oxide gels U-type curves are obtained, water being selectively adsorbed at all concentrations. This denotes that pyridine is more strongly adsorbed by silica than by alumina or ferric oxide gels, a fact which can be correlated with the acidic nature of silica surface.

There is a notable difference also in the behaviour of the three gels towards benzene-carbon tetrachloride mixtures. With silica and ferric oxide gels, there is selective adsorption of benzene throughout and U-type curves are obtained. Alumina gel however gives the S-type curve and in fact the curve indicates for alumina a higher selectivity for carbon tetrachloride. This is presumably due to an attraction between the aluminium of the gel and the chlorine atoms of the adsorbed liquid.

Doss and Rao[6] have suggested that the S-shaped curve is probably caused by the preferential adsorption of molecular compounds of the components of the binary mixture. In agreement with this point of view they found that the mixture giving zero selectivity in pyridine-water-silica system has a composition closely corresponding to the mono-hydrate. We have obtained similar results with carbon tetrachloride-benzene mixtures. The composition of the mixture giving zero selectivity corresponds approximately to C_6H_6, CCl_4. It is interesting to note that alumina gel turns black when immersed in benzene-carbon tetrachloride mixtures, while the gel suffers no such colour change when immersed in either benzene or carbon tetrachloride. On addition of water the gel loses the black colour owing to the desorption of the benzene-carbon tetrachloride mixture. The blackening effect is being investigated in this laboratory.

In conclusion, it may be stated that the adsorption of liquids on gels of silica, alumina and ferric oxide, is not to be looked upon as mere capillary condensation, but that the chemical nature of the gel has a marked influence on selective adsorption from binary mixtures of liquids.

Summary.

The effect of temperature of activation on the capillary space in alumina and ferric oxide gels has been studied. Structural changes in alumina gel have been noticed in the neighbourhood of 500° C. and 900° C. and their significance discussed.

Adsorption on alumina and ferric oxide gels from binary mixtures of liquids has been studied and the behaviour of these has been compared with that of silica. It is concluded that the chemical nature of a gel markedly affects selective adsorption from binary mixtures of liquids.

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